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(54) Title: VINYLAROMATIC POLYMERS WITH IMPROVED FLAME RESISTANCE

(57) Abstract: Vinylaromatic polymers, optionally expandable, with improved flame resistance which comprise: a) a matrix obtained by polymerizing 50-100 % by weight of one or more vinylaromatic monomers and 0-50 % by weight of a copolymerizable monomer; b) 0-10 % by weight, calculated with respect to the polymer (a), of an expanding agent embedded in the polymeric matrix; c) 0.05-2 % by weight, calculated with respect to the polymer (a), of a synergic mixture of additives for flame resistance, comprising a chloro- and/or bromo-substituted hydrocarbon, 2,2-bis(4-allyloxy-3,5-dibromophenyl)-propane and an organic compound capable of generating free radicals at a temperature higher than 130 °C.

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VINYLAROMATIC POLYMERS WITH IMPROVED FLAME RESISTANCE

The present invention relates to vinylaromatic polymers with improved flame resistance.

10 More specifically, the present invention relates to self-extinguishing or flame-resistant vinylaromatic polymers, optionally expandable, capable of complying, for example, with the DIN 4102 regulation for expandable materials.

15 Vinylaromatic polymers, and among these, polystyrene in particular, are products which have been known and used for a long time for the preparation of compact and/or expanded articles which can be used in various applicative fields, among which the most important are those relating
20 to household appliances, transport, the building industry, office machines, etc. A particularly interesting field is thermal insulation where vinylaromatic polymers are essentially used in expanded form.

These expanded products are obtained by swelling in a
25 pre-expander beads of expandable polymer previously impreg-

nated with an expanding agent and molding the swollen particles inside a closed mould by means of the contemporaneous effect of pressure and temperature. The swelling of the particles is generally effected with vapour, or another
5 gas, maintained at a temperature slightly higher than the glass transition temperature (T_g) of the polymer.

A particular applicative field of expanded polystyrene is that of thermal insulation in the building industry where it is generally used in the form of flat plates. For
10 these applications, expanded polystyrene must also have, in addition to a low thermal conductivity, a valid flame resistance which is generally obtained with particular additives.

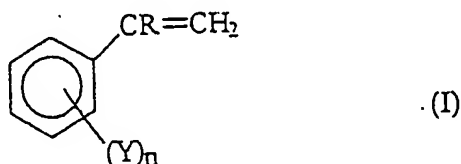
U.S. patent 4,293,656 describes a polystyrene with
15 flame resistant properties obtained by adding to the polymer, a synergic mixture of two halogenated components, one consisting of a chloro- and/or bromo-substituted hydrocarbon, the other of a diallylether of tetrabromobisphenol A such as 2,2-bis(4-allyloxy-3,5-dibromophenyl)-propane.

20 The Applicant has now found that the addition of an organic compound, capable of generating free radicals at a temperature higher than the polymerization temperature of polystyrene, to the synergic mixture of the known art, further improves the flame-resistance properties of the polymer.
25 mer.

An object of the present invention therefore relates to vinylaromatic polymers, optionally expandable, with improved flame resistance which comprise:

- a) a matrix obtained by polymerizing 50-100% by weight of one or more vinylaromatic monomers and 0-50% by weight of a copolymerizable monomer;
- b) 0-10% by weight, calculated with respect to the polymer (a), of an expanding agent embedded in the polymeric matrix;
- c) 0.05-5% by weight, calculated with respect to the polymer (a), of a synergic mixture of additives for flame resistance comprising a chloro- and/or bromo-substituted hydrocarbon, 2,2-bis(4-allyloxy-3,5-dibromophenyl)propane and an organic compound capable of generating free radicals at a temperature higher than 130°C.

The term "vinylaromatic monomer", as used in the present description and claims, essentially refers to a product which corresponds to the following general formula:



wherein R is a hydrogen or a methyl group, n is zero or an integer ranging from 1 to 5 and Y is a halogen, such as chlorine or bromine, or an alkyl or alkoxyl radical having from 1 to 4 carbon atoms.

Examples of vinylaromatic monomers having the general formula defined above are: styrene, α -methylstyrene, methylstyrene, ethylstyrene, butylstyrene, dimethylstyrene, mono-, di-, tri-, tetra- and penta-chlorostyrene, bromo-
5 styrene, methoxy-styrene, acetoxy-styrene, etc. Preferred vinylaromatic monomers are styrene and α -methylstyrene.

The vinylaromatic monomers having general formula (I) can be used alone or in a mixture of up to 50% by weight with other copolymerizable monomers. Examples of these
10 monomers are (meth)acrylic acid, C_1 - C_4 alkyl esters of (meth)acrylic acid, such as methyl acrylate, methylmethacrylate, ethyl acrylate, ethylmethacrylate, isopropyl acrylate, butyl acrylate, amides and nitriles of (meth)acrylic acid such as acrylamide, methacrylamide, ac-
15 rylonitrile, methacrylonitrile, butadiene, ethylene, divinylbenzene, maleic anhydride, etc. Preferred copolymerizable monomers are acrylonitrile and methylmethacrylate.

Any expanding agent capable of being englobed in the vinylaromatic polymeric matrix, can be used in a combina-
20 tion with the vinylaromatic polymers object of the present invention. Typical examples are aliphatic hydrocarbons, freon, carbon dioxide, water, etc.

The synergic mixture of flame-resistance additives substantially comprises three additives. The first consists
25 of a chloro- and/or bromo-substituted hydrocarbon, selected

from linear, branched or cyclic paraffins containing from 5 to 20 carbon atoms and (alkyl)aromatic hydrocarbons containing from 6 to 20 carbon atoms and, optionally, one or more heteroatoms such as oxygen, nitrogen and sulfur. The
5 halogen content in these additives is equal to at least 50% by weight, preferably from 55 to 85%.

Examples of chloro- and/or bromo-substituted hydrocarbons are 1,2,5,6,9,10-hexabromocyclododecane, tetrabromo, dibenzalacetone, pentabromophenylallyl ether, pentabromo-
10 monochlorocyclohexane, 1,1,2,3,4,4-hexabromobutene-2, 2,5-bis(tribromomethyl)-1,3,4-thiadiazole, 2,4,6-tris(tribromomethyl)-1,3,5,-triazine, tetrabromoethane, bromotrichloromethane, 1,2,5,6-tetrabromohexane, hexabromobenzene, pentabromophenol, pentabromo-diphenylether, octabromocyclo-
15 hexadecane, α -bromonaphthalene.

In the synergic mixture of flame-resistance additives the bromo- and/or chloro-substituted hydrocarbon is present in a quantity equal to or higher than 10% by weight, preferably from 10 to 70%, even more preferably from 15 to 50%.

20 The additive 2,2-bis(4-allyloxy-3,5-dibromophenyl)-propane is present in the synergic mixture in a quantity lower than 70% by weight, preferably from 25 to 70%, even more preferably from 30 to 65%.

Any organic compound capable of generating free radicals at a temperature higher than 130°C can be used as
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third component of the synergic mixture of flame-resistance additives, object of the present invention. For example, these additives can be selected from peroxides, percarbonates, azo derivatives or from carbon-carbon initiators.

5 Dicumyl peroxide, 2,3-dimethyl-2,3-diphenyl butane and diphenyl butane, however, are preferred.

The third additive of the synergic mixture is present in a quantity equal to or lower than 30% by weight, preferably from 5 to 25%, even more preferably from 7 to 20%.

10 The expanding agent (b), if present, and the synergic mixture (c) are preferably added to the vinylaromatic polymer during the polymerization phase. At the end of the addition of the mixture, a polymer is obtained which, if expanding agents are added, can be transformed to produce expanded articles having a density ranging from 5 to 50 g/l, preferably from 10 to 25 g/l, with an excellent thermal insulation capacity. These materials, moreover, have a flame-resistance property which passes the DIN 4102 test.

Conventional additives generally used with traditional materials, such as pigments, stabilizing agents, mineral fillers of athermane materials, such as graphite or carbon black, or refracting and/or reflective materials such as titanium dioxide, antistatic agents, detaching agents, etc., can be added to the vinylaromatic polymers, optionally expandable, object of the present invention.

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A further object of the present invention relates to the process for the preparation of vinylaromatic polymers, optionally expandable, with improved flame-resistance.

In particular, a further object of the present invention relates to a process for preparing vinylaromatic polymers, optionally expandable, which comprises polymerizing in an aqueous suspension one or more vinylaromatic monomers, optionally together with at least one polymerizable comonomer in a quantity of up to 50% by weight, in the presence of a synergic mixture of flame-resistance additives comprising a chloro- and/or bromo-substituted hydrocarbon, 2,2-bis(4-allyloxy-3,5-dibromophenyl)-propane and an organic compound capable of generating free radicals at a temperature higher than 130°C, and from 0 to 10% by weight of an expanding agent added before, during or after the end of the polymerization.

At the end of the polymerization, substantially spherical polymer beads are obtained, with an average diameter ranging from 0.2 to 2 mm, inside which the synergic mixture is homogeneously dispersed.

During the polymerization in suspension, polymerization additives, typically used for producing vinylaromatic polymers, are adopted, such as polymerization catalysts, stabilizing agents of the suspension, chain transfer agents, expanding aids, nucleating agents, plasticizers,

mineral fillers, etc. In particular, in the case of expand-
able polymers, it is preferable to add mineral fillers of
athermane materials, such as graphite, or refracting mate-
rials, such as titanium dioxide, during the polymerization,
5 in a quantity ranging from 0.05 to 25% by weight, calcu-
lated with respect to the resulting polymer.

The expanding agents, if present, are preferably added
during the polymerization phase and are selected from ali-
phatic or cycloaliphatic hydrocarbons containing from 3 to
10 6 carbon atoms such as n-pentane, isopentane, cyclopentane
or their mixtures; the halogenated derivatives of aliphatic
hydrocarbons containing from 1 to 3 carbon atoms such as,
for example, dichlorodifluoromethane, 1,2,2-trifluoro-
ethane, 1,1,2-trifluoroethane; carbon dioxide and water.

15 To improve the stability of the suspension, it is pos-
sible to use a solution of vinylaromatic polymer in the
monomer, or mixture of monomers, in which the concentration
of polymer ranges from 1 to 30% by weight, preferably from
5 to 20%. The solution can be obtained either by diluting a
20 preformed polymer (for example fresh polymer or the waste
products of previous polymerizations and/or expansions) in
the monomer or by pre-polymerizing the monomer, or mixture
of monomers, in mass, in order to obtain the above concen-
trations, and then continuing the polymerization in aqueous
25 suspension in the presence of the remaining additives.

Another object of the present invention relates to a process for preparing in mass and in continuous, vinylaromatic polymers, optionally expandable, which comprises the following steps in series:

- 5 i. feeding a vinylaromatic polymer, as described above, to an extruder, together with the synergic mixture of flame-resistance additives;
- ii. heating the vinylaromatic polymer to a temperature higher than the relative melting point;
- 10 iii. injecting possible additives such as expanding agents, into the molten polymer before extrusion through a die; and
- iv. forming beads, optionally expandable, through a die, in a substantially spherical form with an average diameter ranging from 0.2 to 2 mm.

15 A detailed method for preparing vinylaromatic polymers in mass and in continuous is provided in European patent EP 126,459.

In the case of expandable vinylaromatic polymers, 20 whether they be prepared in suspension or in mass and in continuous, at the end of the polymerization, the beads produced are subjected to pre-treatment generally applied to traditional materials and which essentially consists in:

1. coating the beads with a liquid antistatic agent such as

25 amines, tertiary ethoxylated alkylamines, ethylene ox-

ide-propylene oxide copolymers, etc. The purpose of this agent is to facilitate both the adhesion of the coating and also the screening of the beads prepared in suspension;

- 5 2. applying the coating to the above beads, said coating essentially consisting of a mixture of mono-, di- and tri-esters of glycerin (or other alcohols) with fatty acids and of metallic stearates such as zinc stearate.

Some illustrative but non-limiting examples are provided for a better understanding of the present invention and for its embodiment.

EXAMPLES 1-7

A mixture of 150 parts by weight of water, 0.1 parts of sodium pyrophosphate, 100 parts of styrene, 0.15 parts of benzoyl peroxide, 0.25 parts of ter-butyl perbenzoate and a synergic mixture of flame-resistance additives comprising hexabromine-cyclododecane (EBCD) and 2,2-bis(4-allyloxy-3,5-dibromophenyl)-propane (BE) (0.53% of total bromine) and 0.2 parts of dicumyl peroxide (DCP) in the proportions indicated in the following table, are charged into a closed, stirred container. The mixture is heated to 90°C under stirring.

After about 2 hours at 90°C, 4 parts of a solution at 10% of polyvinylpyrrolidone are added. The mixture is heated, under stirring, for a further 2 hours to 100°C, 7

parts of a 70/30 mixture of n-pentane and i-pentane are added and the mixture heated for a further 4 hours to 125°C.

The beads of expandable polymer thus produced are subsequently recovered, washed with deionized water, dried in a stream of warm air, 0.02% of ethoxylated amine are added, and screened separating the fraction with a diameter ranging from 1 to 1.5 mm.

0.2% of glycerylmonostearate and 0.05% of zinc stearate are then added to the fraction.

The beads are expanded with vapour to a temperature of 100°C and subsequently moulded to give simple end-products with a density of about 16-17 g/l. Test samples according to the regulation DIN 4102 are taken from the end-products. These test samples are then conditioned in an oven up to the maximum expanding content of 0.5%. The results of the flame test are indicated in the table.

TABLE

TEST	EBCD %	BE %	DCP %	H _{flame} (1) cm	t _{average} (2) sec	Notes
1	0.67	-	0.2	7.4	7.0	
2	0.64	0.2	-	8.0	4.9	
3	0.64	0.2	0.2	3.0	2.8	
4	0.17	0.74	0.2	3.4	4.7	
5	0.34	0.49	0.2	3.6	4.4	
6	0.51	0.25	0.2	5.6	5.5	
7	0.32	0.10	0.2	9.0	8.5	(3)

- (1) flame height
- (2) average combustion time
- (3) minimum quantity for passing the DIN 4102 test

EXAMPLE 8

5 The same procedure is substantially adopted as in the previous examples except that the dicumyl peroxide of Example 5 is substituted with 2,3-dimethyl-2,3-diphenyl butane (Perkadox 30 of AKZO).

10 When subjected to the flame test, the sample gave the following results:

$H_{\text{flame}} = 3.3 \text{ cm};$

$t_{\text{average}} = 3.7 \text{ sec.}$

CLAIMS

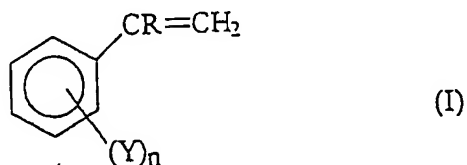
1. Vinylaromatic polymers, optionally expandable, with improved flame resistance, which comprise:

a) a matrix obtained by polymerizing 50-100% by weight of one or more vinylaromatic monomers and 0-50% by weight of a copolymerizable monomer;

b) 0-10% by weight, calculated with respect to the polymer (a), of an expanding agent embedded in the polymeric matrix;

c) 0.05-5% by weight, calculated with respect to the polymer (a), of a synergic mixture of additives for flame resistance comprising a chloro- and/or bromo-substituted hydrocarbon, 2,2-bis(4-allyloxy-3,5-dibromophenyl)propane and an organic compound capable of generating free radicals at a temperature higher than 130°C.

2. The polymers according to claim 1, wherein the vinylaromatic monomer is selected from those corresponding to the following general formula:



wherein R is a hydrogen or methyl group, n is zero or an integer ranging from 1 to 5 and Y is a halogen, such as chlorine or bromine, or an alkyl or alkoxy

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radical having from 1 to 4 carbon atoms.

3. The polymers according to claim 1 or 2, wherein the vinylaromatic monomers having general formula (I) are styrene and α -methylstyrene.

5 4. The polymers according to any of the previous claims, wherein the vinylaromatic monomers having general formula (I) are used in a mixture, of up to 50% by weight, with other copolymerizable monomers selected from (meth)acrylic acid, C₁-C₄ alkyl esters of
10 (meth)acrylic acid, amides and nitriles of (meth)acrylic acid, butadiene, ethylene, divinylbenzene, maleic anhydride.

5. The polymers according to claim 4, wherein the copolymerizable monomers are acrylonitrile and methyl-
15 methacrylate.

6. The polymers according to any of the previous claims, wherein the chloro- and/or bromo-substituted hydrocarbon of the synergic mixture of flame-resistance additives is selected from linear, branched or cyclic paraffins containing from 1 to 20 carbon atoms and (alkyl)aromatic hydrocarbons containing from 6 to 20 carbon atoms and, optionally, one or more heteroatoms
20 such as oxygen, nitrogen and sulfur.

7. The polymers according to any of the previous claims,
25 wherein the halogen content in the chloro- and/or

bromo-substituted hydrocarbon is equal to at least 50% by weight, preferably from 55 to 85%.

8. The polymers according to claim 6 or 7, wherein the chloro- and/or bromo-substituted hydrocarbons are selected from 1,2,5,6,9,10-hexabromocyclododecane, tetrabromo dibenzalacetone, pentabromophenylallyl ether, pentabromomonochlorocyclohexane, 1,1,2,3,4,4-hexabromobutene-2,2,5-bis(tribromomethyl)-1,3,4-thiadiazole, 2,4,6-tris(tribromomethyl)-1,3,5-triazine, tetrabromoethane, bromotrichloromethane, 1,2,5,6-tetrabromohexane, hexabromobenzene, pentabromophenol, pentabromodiphenylether, octabromocyclohexadecane, α -bromonaphthalene.
9. The polymers according to any of the previous claims, wherein in the synergic mixture of flame-resistance additives, the bromo- and/or chloro-substituted hydrocarbon is present in a quantity equal to or higher than 10% by weight, preferably from 10 to 70%.
10. The polymers according to any of the previous claims, wherein the additive 2,2-bis(4-allyloxy-3,5-dibromophenyl)-propane is present in the synergic mixture in a quantity equal to or lower than 70% by weight, preferably from 25 to 70%.
11. The polymers according to any of the previous claims, wherein the organic compound capable of generating

free radicals at a temperature higher than 130°C is selected from peroxides, percarbonates, azo derivatives or from carbon-carbon initiators.

12. The polymers according to claim 11, wherein the organic compound is selected from dicumyl peroxide, 2,3-dimethyl-2,3-diphenyl butane and diphenyl butane.

13. The polymers according to any of the previous claims, wherein the organic compound capable of generating free radicals at a temperature higher than 130°C is present in the synergic mixture in a quantity equal to or lower than 30% by weight, preferably from 5 to 25%.

14. Expanded articles obtained with the expandable vinylaromatic polymers according to any of the previous claims, having a density ranging from 5 to 50 g/l, with a flame-resistance property which is such as to enable it to pass the DIN 4102 test and a thermal conductivity ranging from 25 to 50 mW/mK.

15. A process for the preparation of polymers, optionally expandable, with improved flame resistance which comprises polymerizing in an aqueous suspension one or more vinylaromatic monomers, optionally together with at least one polymerizable comonomer in a quantity of up to 50% by weight, in the presence of a synergic mixture of flame-resistance additives comprising a chloro- and/or bromo-substituted hydrocarbon, 2,2-

bis(4-allyloxy-3,5-dibromophenyl)-propane and an organic compound capable of generating free radicals at a temperature higher than 130°C, and 0-10% by weight of an expanding agent added before, during or after the end of the polymerization.

16. A process for preparing in mass and in continuous, vinylaromatic polymers, optionally expandable, which comprises the following steps in series:

i. feeding a vinylaromatic polymer, as described above, to an extruder, together with the synergic mixture of flame-resistance additives;

ii. heating the vinylaromatic polymer to a temperature higher than the relative melting point;

iii. injecting possible additives such as expanding agents, into the molten polymer before extrusion through a die; and

iv. forming beads, optionally expandable, through a die, in a substantially spherical form with an average diameter ranging from 0.2 to 2 mm.

17. The process according to claim 15 or 16, wherein at the end of the polymerization, substantially spherical beads of polymer are obtained, with an average diameter ranging from 0.2 to 2 mm, inside which the synergic mixture is homogeneously dispersed.

18. The process according to claim 15, 16 or 17, wherein

during the polymerization, polymerization additives are used, selected from polymerization catalysts, stabilizing agents of the suspension, chain transfer agents, expanding aids, nucleating agents, plasticizers, mineral fillers.

19. The process according to claim 18, wherein the mineral filler is selected from athermane or refracting materials in a quantity ranging from 0.05 to 25% by weight calculated with respect to the resulting polymer.

20. The process according to claim 15, wherein the expanding agents are added during the polymerization phase.

21. The process according to claim 15, wherein the polymerization takes place using a solution of vinylaromatic polymer in the monomer, or mixture of monomers, wherein the concentration of polymer ranges from 1 to 30% by weight.

22. The process according to any of the previous claims from 15 to 21, wherein the expandable beads are subjected to pretreatment applied to conventional expandable beads and which essentially consists in:

1. coating the beads with a liquid antistatic agent such as amines, tertiary ethoxylated alkylamines, ethylene oxide-propylene oxide copolymers;

2. applying the coating to the above beads, said coating essentially consisting of a mixture of mono-,

di- and tri-esters of glycerin with fatty acids and of
metallic stearates such as zinc stearate.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F2/44 C08K5/03 C08K5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 032 993 A (BASF AG.) 5 August 1981 (1981-08-05) cited in the application ---	
A	US 3 058 926 A (J. EICHORN) 16 October 1962 (1962-10-16) -----	

☐ Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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